

Accurate first principles detailed balance determination of Auger recombination and impact ionization rates in semiconductors

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Abstract

The technologically important problem of predicting Auger recombination lifetimes in semiconductors is addressed by means of a fully first-principles formalism. The calculations employ highly precise energy bands and wave functions provided by the full-potential linearized augmented plane wave (FLAPW) code based on the screened exchange local density approximation. The minority carrier Auger lifetime is determined by two closely related approaches: *i*) a direct evaluation of the Auger rates within Fermi's Golden Rule, and *ii*) an indirect evaluation, based on a detailed balance formulation combining Auger recombination and its inverse process, impact ionization, in a unified framework. Calculated carrier lifetimes determined with the direct and indirect methods show excellent consistency *i*) between them for *n*-doped GaAs and *ii*) with measured values for GaAs and InGaAs. This demonstrates the validity and accuracy of the computational formalism for the Auger lifetime and indicates a new sensitive tool for possible use in materials performance optimization.

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Led by advances in computational simulation, the paradigm within semiconductor device engineering is shifting away from the static perspective of material properties as design “constraints” towards a more empowering view of material properties as design optimization parameters. This growing trend is evident clearly in recent initiatives in nano-engineered materials from quantum dots, quantum wells and nanowires to band structure engineering of conventional [1] and ordered superlattice [2] materials. However, despite the fundamental importance of these processes, owing to a lack of adequate capability for their prediction, carrier recombination processes in semiconductors have remained largely beyond the reach of materials design. Minority carrier lifetime is a critical, performance-limiting material parameter in many opto-electronic devices, as well as in bipolar transistors, $p - n$ rectifiers and thyristors. Two recombination processes - radiative and Auger - generally impose theoretical and practical limits on carrier lifetimes. Minority carrier lifetimes in heavily doped and/or narrow band gap materials (such as 1.6 μm $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ - a basic material for thermophotovoltaic devices) tend to be limited by Auger recombination (AR), and so its first-principles determination is the focus of this paper.

In n -doped, direct band gap materials, the dominant Auger process is electron-electron-hole (e^-e^-h) recombination[3]. As shown in Fig. ?? (a), in the e^-e^-h process, a valence band hole decays via non-radiative recombination with a conduction band electron, conserving energy and momentum through transfer to a second conduction band electron. This process commonly is referred to as the conduction-conduction-conduction-“heavy hole” (CCCH) process. In the inverse process of electron-initiated impact ionization (I-I), depicted in Fig. ?? (b), an energetic primary electron promotes a secondary valence band electron into the conduction band, producing a mobile electron-hole pair. Processes closely analogous to those depicted in Fig. ?? (a) and (b) occur in p -type materials, resulting in an electron decay through a “conduction electron”-“heavy hole”-“heavy hole”-“light hole” (CHHL) AR and in a hole-initiated I-I, respectively.

In this work, the fully first-principles approach that was used successfully to evaluate I-I rates [4] is extended to the calculation of AR rates which are found to be in good agreement with previous experimental and theoretical values reported for the most studied semiconductor - n -type GaAs - and for technologically important InGaAs. Moreover, AR lifetimes calculated directly via Fermi’s Golden Rule are shown to be strikingly consistent with lifetime values determined via detailed balance principles proceeding from calculated I-I rates.

To our knowledge, this density functional theory (DFT[5]) study represents the first fully ab initio determination of Auger recombination lifetimes. The agreement of computational results with experiment for n -type GaAs and $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$ indicates that this method is sufficiently precise and reliable to be able to correctly predict trends of the Auger coefficient as a function of physical parameters, such as doping, composition, etc. Since the current approach is all-electron and ab initio in nature, we expect the same methods to be equally successful for new and more complex materials. Finally, we find that detailed balance evaluations proceeding from I-I rate calculations appear to be a computationally efficient means of determining AR rates.

Within an independent particle scheme[6], given a hole in state (n_2, \mathbf{k}_2) , the AR rate is expressed as:

$$R^{AR}(n_2, \mathbf{k}_2) = 2\frac{2\pi}{\hbar} \sum_{n_3, n_4} \int d^3\mathbf{k}_3 \int d^3\mathbf{k}_4 |M|^2 f(E_{\mathbf{k}_4}^{n_4}) f(E_{\mathbf{k}_3}^{n_3}) g(E_{\mathbf{k}_1}^{n_1}) \delta(E_{\mathbf{k}_3}^{n_3} + E_{\mathbf{k}_4}^{n_4} - E_{\mathbf{k}_1}^{n_1} - E_{\mathbf{k}_2}^{n_2}) \quad (1)$$

and the total AR rate is:

$$R^{AR} = \sum_{n_2} \int d^3\mathbf{k}_2 g(E_{\mathbf{k}_2}^{n_2}) R^{AR}(n_2, \mathbf{k}_2) \quad (2)$$

Here, the n_i are the band indices ($n_i, i = 1, \dots, 7$ ($i = 5, \dots, 11$) for GaAs (InGaAs), corresponding to the four valence and three conduction bands considered) and $\mathbf{k}_{1,3,4}$ are \mathbf{k} points in the full Brillouin zone (BZ) [7]. The many-fold integration over the BZ is performed according to the Sano–Yoshii scheme[8], using 152 [9] and 126 \mathbf{k} points in the irreducible wedge of the zincblende and tetragonal Brillouin zone, respectively [10]. The summation over \mathbf{k}_2 (Eq.2) is carried out in the irreducible wedge of the zone. Energy conservation is enforced through the δ function in the energy eigenvalues; f denotes the Fermi–Dirac occupation probability and $g = 1 - f$. The matrix elements, taking into account both *direct* and *exchange* terms (obtained from the direct contribution through the exchange of final states), are of the form: $|M|^2 = \frac{1}{2}(|M_D|^2 + |M_E|^2 + |M_D - M_E|^2)$. The direct term is given as:

$$M_D = \frac{4\pi e^2}{\Omega} \sum_{\mathbf{G}_0, \mathbf{G}_U} \delta(\mathbf{k}_3 + \mathbf{k}_4 - \mathbf{k}_1 - \mathbf{k}_2 + \mathbf{G}_0) \quad (3)$$

$$\frac{\rho_{n_3, \mathbf{k}_3; n_1, \mathbf{k}_1}(\mathbf{G}_U) \rho_{n_4, \mathbf{k}_4; n_2, \mathbf{k}_2}(\mathbf{G}_0 - \mathbf{G}_U)}{\varepsilon(q)(|\mathbf{k}_1 - \mathbf{k}_3 + \mathbf{G}_U|^2 + \lambda^2)}$$

where e is the electronic charge and Ω is the volume of the unit cell. Momentum conservation is enforced through the δ function in the \mathbf{k} vectors and $\rho_{n_f, \mathbf{k}_f; n_i, \mathbf{k}_i}(\mathbf{G})$ is the Fourier transform of the overlap matrix of the wave functions, *i.e.*, $\rho_{n_f, \mathbf{k}_f; n_i, \mathbf{k}_i}(\mathbf{r}) = \Psi_{n_f, \mathbf{k}_f}^*(\mathbf{r}) \Psi_{n_i, \mathbf{k}_i}(\mathbf{r})$. The subscripts i and f denote initial and final states; $q = |\mathbf{k}_1 - \mathbf{k}_3 + \mathbf{G}_U|$ is the momentum transfer and \mathbf{G}_0 and \mathbf{G}_U are reciprocal lattice vectors. To describe the interaction between the valence and conduction band electrons, we used a Coulomb interaction screened through a static dielectric function proposed by Cappellini *et al.*, $\varepsilon(q)$ [11], that has been shown to be very accurate for semiconductors. The interaction between conduction band carriers is modeled through a Debye potential (screened Coulomb interaction), in which the inverse of the screening length is expressed as $\lambda = \sqrt{\frac{4\pi n^0 e^2}{K_B T}}$, n^0 , T and K_B being the carrier density, the temperature (here, $T=300$ K) and the Boltzmann constant, respectively.

The theoretical estimate of the I-I rate[12, 13] is known to be quite sensitive to the assumed band structure. Therefore, the importance of employing accurate quasi-particle bands as a basis for I-I and AR calculations needs to be emphasized. To faithfully reproduce experimental band structures (both occupied and virtual states), we employ the screened-exchange local density approximation (sX-LDA)[14, 15], as implemented[16] self-consistently in the highly precise, all-electron, full-potential linearized augmented plane wave (FLAPW)[17] method. The sX-LDA approach corrects known deficiencies of the LDA for excited states and has been shown to be very successful for treating a large variety of semiconductors[1, 16].

The effect of spin-orbit coupling, neglected here, was investigated in Ref.[13] for GaAs; the overall effect was shown to be relatively small. Umklapp processes for $\mathbf{G}_U = 0$ were fully included in our calculations; the $\mathbf{G}_0 \neq 0$ terms, which are important at high energies were not included, since Auger is a threshold process. Phonon-assisted transitions[18, 19] and many-body[20, 21] effects were also not included; for InGaAs, Dutta and Nelson [19] showed that phonon assisted AR should not be relevant compared to the direct AR. Within these approximations, giving an estimated overall error of 30-40 % on the AR rates, we show below that our simple band-to-band AR within DFT correctly describes the physical trends as a function of several technological parameters, and so may be used as a sensitive tool in materials device optimization.

It can be shown [22], for band gaps $E_{gap} \gg K_B T$, that the Auger partial lifetime can be expressed as

$$\frac{1}{\tau_p} = \frac{R^{AR}}{N_p^0} \quad (4)$$

where N_p^0 is the number of minority carriers per unit cell at equilibrium (N_p^0/Ω corresponds to the minority carrier density p)[22]. In Fig.?? we show the dependence of the calculated hole Auger lifetime on carrier density, which is approximately linear on a log-log scale. Similar trends have been reported, for example, in an empirical pseudopotential study of AR in Si [6] and in a recent experimental study of AR in n -doped InGaAs [23].

The Auger coefficient, C_n , is defined by the relation:

$$\frac{1}{\tau_p} = C_n (n^0)^2 \quad (5)$$

Recall that partial recombination lifetimes usually are “determined” experimentally based on curve fits to carrier lifetime measurements resulting from several competing recombination processes. The parabolic relationship above is the usual basis for determinations of the Auger recombination coefficient. It is noted, however, [6] that both shifts in the Fermi energy (particularly pronounced in many III-V alloys with low effective masses), and changes in the Debye screening length introduce a carrier density dependence into Eqs.1 and 2, so that C_n itself is expected to depend on n . This is actually the case from our calculations. Indeed, in GaAs our C_n , determined as the ratio of the inverse lifetime and the carrier density squared, ranges from $2.3 \times 10^{-30} \text{ cm}^{-6} \text{ s}^{-1}$ at $n \sim 4 \times 10^{15} \text{ cm}^{-3}$ to $0.5 \times 10^{-30} \text{ cm}^{-6} \text{ s}^{-1}$ at $n \sim 6 \times 10^{16} \text{ cm}^{-3}$. This range of values is compared in Table I with previously reported experimental[24, 25, 26] and theoretical[27, 28] results. In InGaAs, there is only a slight dependence of C_n on n , C_n ranging from $0.8 \times 10^{-29} \text{ cm}^{-6} \text{ s}^{-1}$ to $1.1 \times 10^{-29} \text{ cm}^{-6} \text{ s}^{-1}$ for concentrations ranging from $7 \times 10^{16} \text{ cm}^{-3}$ to $2 \times 10^{18} \text{ cm}^{-3}$. These values are compared in Table II with previous experimental [23, 29, 30] and theoretical [31, 32] results. The comparison between the calculated values for the binary and the ternary compound shows that there is a strong reduction (by an order of magnitude) of C_n , suggesting that the Auger process is crucial in the narrow-gap InGaAs. Despite the wide range over which the reported Auger coefficients vary, the calculated trend with Ga content is confirmed experimentally, unambiguously emphasizing the power of DFT in predicting both quantitatively and qualitatively correct physical trends as a function of doping, pressure, composition, etc. The wide range

of reported Auger coefficients suggests the complexity of both the measurements and the calculations. Our result for the Auger coefficient is in good agreement with most of the published experimental values and is again consistent, when compared, with previously reported results from model calculations incorporating various simplifications (such as constant effective masses [27, 28]). All considered, we conclude that our results confirm the reliability of the computational methods and band structures herein described *i)* to accurately calculate Auger recombination lifetimes that cannot be easily or unambiguously determined by experiment; *ii)* for mapping trends with respect to material composition and dopant density, that are useful to guide optoelectronic device and materials design; and *iii)* for describing Auger recombination in novel and more complex materials.

Auger recombination and impact ionization are related as inverse microscopic processes through the principle of detailed balance (PDB), in the same manner as optical emission and absorption. In fact, in the radiative (non-radiative) case, the $e - h$ generation process is the absorption (I-I), in which the initial object is the photon (highly energetic impacting electron); correspondingly, their inverse recombination process is emission (AR), in which the final product is the photon (Auger electron).

Following Landsberg[3], the AR lifetime is given by,

$$\frac{1}{\tau_p} \sim \frac{1}{N_p^0} \sum_{n_1} \int d^3\mathbf{k}_1 \beta(n_1, \mathbf{k}_1) R^{I-I}(n_1, \mathbf{k}_1) f(n_1, \mathbf{k}_1) \quad (6)$$

where $\beta(n_1, \mathbf{k}_1)$ is a factor (≤ 1) that takes into account the occurrence of processes from state (n_1, \mathbf{k}_1) other than I-I and the $R^{I-I}(n_1, \mathbf{k}_1)$ are the I-I rates. This last expression is the non-radiative equivalent of the van Roosbroeck–Shockley relation [33], that has been used extensively in determinations of radiative recombination lifetimes from the complex dielectric function. However, while experimental dielectric function data (or equivalently, refractive index and extinction coefficient data) are abundant and highly reliable, experimental data for electron-initiated impact ionization rates are normally inadequate to estimate the AR lifetime from Eq. (6). A utility of the current formalism is that one can calculate both I-I rates and AR rates either independently from first principles, or from one another via detailed balance arguments. In our formalism, we focus on two selected processes (I-I and AR), each being the inverse of the other; therefore, the PDB holds with $\beta(n_1, \mathbf{k}_1) = 1$ (or, equivalently, that every energetic electron in state (n_1, \mathbf{k}_1) initiates an impact ionization

process). In Fig. ??, Eq. (6) is applied to the previously calculated I-I rates (see [4] for details) and the Auger lifetime for $n^0 = 1.0 \times 10^{16} \text{ cm}^{-3}$ is derived. The open symbol in Fig. ?? denotes the value obtained, which is in striking agreement with the values calculated using the direct approach (see Eq.1). The excellent agreement achieved between the direct and "indirect" calculations of both parameters provides confidence in the equivalency of the two approaches and in the numerical procedures embodied therein.

In summary, we have presented a fully first-principles formalism for calculating Auger recombination lifetimes using screened exchange FLAPW quasiparticle wavefunctions and band structures determined self-consistently. The numerical accuracy of the approach was checked using the principle of detailed balance applied to the two simulated processes, I-I and AR. The Auger lifetime was determined using two equivalent approaches, "direct" and "indirect," with highly consistent results. Our results for GaAs and InGaAs are in excellent agreement with the most accurate experimental and theoretical data, providing confidence in the computational method and justifying its future applications to more complex systems.

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TABLE I: Auger coefficients in n -type GaAs. The sX-LDA FLAPW results are given to cover the range of possible C_n values.

Exp.technique or theor.approach	C_n (cm ⁶ s ⁻¹)
sX-LDA FLAPW	$(0.5 \leq C_n \leq 2.3) \cdot 10^{-30}$
Photoacoustic determination ^a	$1.3 \cdot 10^{-30}$
Time-resolved photoluminescence decay ^b	$(7 \pm 4) \cdot 10^{-30}$
Time-resolved photoluminescence decay ^c	upper limit of $1.6 \cdot 10^{-29}$
non-parab. bands + phonon-assisted + eff. masses ^d	$4.7 \cdot 10^{-30}$
non-parab. bands + phonon-assisted + $\mathbf{k} \cdot \mathbf{p}$ ^e	$1.5 \cdot 10^{-31}$

a. Ref. 26

b. Ref. 25

c. Ref. 24

d. Ref. 28

e. Ref. 27

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TABLE II: Auger coefficients in n -type InGaAs.

Exp.technique or theor.approach	C_n (cm^6s^{-1})
sX-LDA FLAPW	$(0.8 \leq C_n \leq 1.1) \cdot 10^{-29}$
Time-resolved photoluminescence decay ^a	$0.5 \cdot 10^{-29}$
Radio-frequency photoconductive decay ^b	$7 \cdot 10^{-29}$
Photoluminescence photon-counting ^c + degenerate carrier conditions	$18 \cdot 10^{-29}$
non-parab. bands + phonon-assisted + eff. masses ^d	$0.5 \cdot 10^{-29}$
Kane model for wave functions ^e	$3 \cdot 10^{-29}$

a. Ref. 29

b. Ref. 30

c. Ref. 23

d. Ref. 31

e. Ref. 32

Simulated processes in n -type materials: (a) Auger recombination, resulting in a hole-decay; (b) electron initiated impact ionization, resulting in a pair production.

Calculated hole Auger lifetime vs carrier concentration in (a) GaAs and (b) InGaAs. The results for the binary compound are obtained according to the direct approach (see Eqs.(2-5) - filled circles) and to the indirect approach (see Eq.(6) - open circle).